

Magnetic State of the Geometrically Frustrated Quasi-One-Dimensional Spin System $\text{Cu}_3\text{Mo}_2\text{O}_9$ Studied by Thermal Conductivity

Koki Naruse^{1*}, Takayuki Kawamata^{1†}, Masumi Ohno¹, Yoshiharu Matsuoka¹,
Masashi Hase², Haruhiko Kuroe³, Tomoyuki Sekine³, Kunihiro Oka⁴, Toshimitsu Ito⁴,
Hiroshi Eisaki⁴, Takahiko Sasaki⁵, and Yoji Koike¹

¹*Department of Applied Physics, Tohoku University, Sendai 980-8579, Japan*

²*National Institute for Materials Science (NIMS), Tsukuba 305-0047, Japan*

³*Department of Physics, Sophia University, Tokyo 102-8554, Japan*

⁴*National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba
305-8501, Japan*

⁵*Institute for Materials Research (IMR), Tohoku University, Sendai 980-8577, Japan*

We have measured the thermal conductivity of the geometrically frustrated quasi-one-dimensional spin system $\text{Cu}_3\text{Mo}_2\text{O}_9$ in magnetic fields. A contribution of the thermal conductivity due to spins has been observed in the thermal conductivity along the spin chains. The thermal conductivity due to phonons, κ_{phonon} , has been found to decrease by the application of a magnetic field, which has been explained as being due to the reduction in the spin gap originating from the spin-singlet dimers. Moreover, it has been found that κ_{phonon} increases with increasing field in high fields above ~ 7 T at low temperatures. This suggests the existence of a novel field-induced spin state and is discussed in terms of the possible spin-chirality ordering in a frustrated Mott insulator.

*Present address: Institute for Materials Research (IMR), Tohoku University, Sendai 980-8577, Japan

†E-mail: tkawamata@teion.apph.tohoku.ac.jp

1. Introduction

The thermal conductivity in low-dimensional quantum spin systems has attracted great interest, because a large amount of thermal conductivity due to spins, namely, magnetic excitations, κ_{spin} , has been observed along the direction where the antiferromagnetic (AF) exchange interaction is strong. In the AF spin-chain systems Sr_2CuO_3 ¹⁻³ and SrCuO_2 ^{1,4} and the two-leg spin-ladder system $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$,⁵⁻⁹ for example, the thermal conductivity due to spinons and magnons, which are magnetic excitations in these systems, has been observed, respectively. In addition, the thermal conductivity has attracted considerable interest, because it is closely related to the magnetic state. That is, the thermal conductivity exhibits a marked change according to the change in the magnetic state, owing to the marked change in the scattering of heat carriers by magnetic excitations. In the spin-Peierls system CuGeO_3 ^{10,11} and the two-dimensional spin-dimer system $\text{SrCu}_2(\text{BO}_3)_2$,^{12,13} the thermal conductivity due to phonons, κ_{phonon} , has been found to be enhanced at low temperatures below the temperature comparable to the spin-gap energy owing to the reduction in the phonon-spin scattering rate and to be suppressed by the application of a magnetic field because of the reduction in the spin gap.^{12,13} Furthermore, a marked enhancement of the thermal conductivity has been observed at low temperatures below the AF transition temperature, T_N , in several AF spin systems.¹⁴⁻²⁰ In the frustrated spin system $\text{Dy}_2\text{Ti}_2\text{O}_7$, recently, the thermal conductivity has been found to be affected by the change in the state of magnetic monopoles, which are magnetic excitations in this system.^{21,22} Accordingly, the thermal conductivity is recognized as a very useful probe to detect a change in the magnetic state and a phase transition.

The compound $\text{Cu}_3\text{Mo}_2\text{O}_9$ is a quasi-one-dimensional spin system with the quantum spin number $S = 1/2$ of Cu^{2+} ions. As shown in Fig. 1(a), distorted tetrahedral spin-chains composed of spin chains of Cu1 and spin dimers of Cu2 and Cu3 run along the b -axis. The spin chains are arranged in the ac -plane as shown in Fig. 1(b). Cu^{2+} spins interact with one another by AF superexchange interactions, whose magnitude has been estimated from the inelastic neutron-scattering experiment as follows.^{23,24} Both the interaction between Cu1 and Cu2, J_1 , and that between Cu1 and Cu3, J_2 , are ~ 19 K. The intradimer interaction between Cu2 and Cu3, J_3 , which is equal to the spin-gap energy, Δ , of the spin dimers, is ~ 67 K. The intrachain interaction between Cu1's, J_4 , is ~ 46 K. The interchain interaction is as negligibly weak as ~ 2.2 K.

The magnetization and specific heat measurements have revealed that $\text{Cu}_3\text{Mo}_2\text{O}_9$ undergoes an AF transition accompanied by weak ferromagnetism (WF) due to the Dzyaloshinsky-

Moriya interaction at 8 K.²⁵ In the AF ordered state, the dispersion branch of magnetic excitations of the spin dimers remains together with that of the AF order^{23,24} and the direction of Cu1 spins is almost parallel to the b -axis but is slightly canted from the b -axis.²⁵ Although canted components of the magnetic moments are in disorder in zero field, they are ordered by the application of a magnetic field of 0.1 T along the a -axis and of 0.8 T along the c -axis. In the AF ordered state, furthermore, it has been found from dielectric constant and magnetization measurements that $\text{Cu}_3\text{Mo}_2\text{O}_9$ shows magnetic and ferroelectric orders simultaneously without any magnetic superlattice formation,²⁶ which has been understood as being due to the possible charge redistribution in a frustrated Mott insulator.^{26–28} The direction of

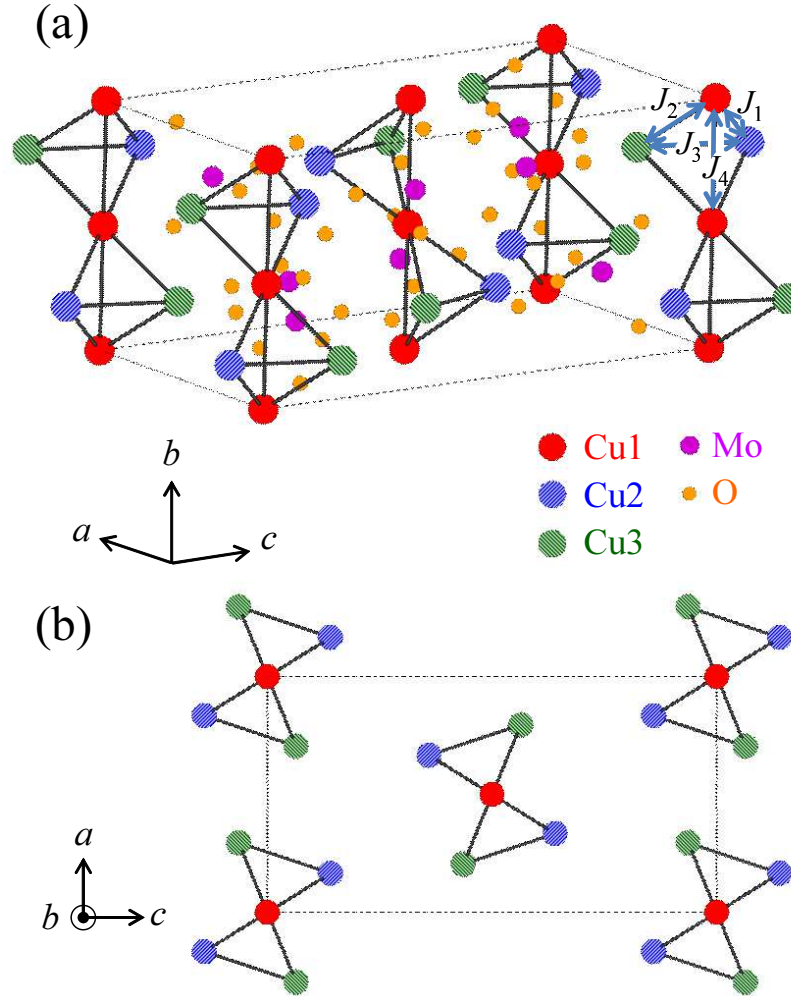


Fig. 1. (Color online) (a) Crystal structure of $\text{Cu}_3\text{Mo}_2\text{O}_9$. Distorted tetrahedral spin-chains run along the b -axis. (b) Crystal structure viewed from the b -axis. Dashed lines indicate the unit cell containing two distorted tetrahedral spin-chains.

the spontaneous electric polarization changes from the c -axis to the a -axis by the application of a magnetic field of ~ 8 T along the c -axis,²⁶ which has been also observed in the electron-spin-resonance spectrum of the powder sample.²⁹ At present, the phase diagram of $\text{Cu}_3\text{Mo}_2\text{O}_9$ in magnetic fields at low temperatures is as shown in Fig. 2.^{26,30,31} Nevertheless, the magnetic state of $\text{Cu}_3\text{Mo}_2\text{O}_9$ has not yet been clarified completely. Accordingly, we have measured the thermal conductivity of single-crystal $\text{Cu}_3\text{Mo}_2\text{O}_9$ in magnetic fields, in order to investigate the magnetic state of $\text{Cu}_3\text{Mo}_2\text{O}_9$ as well as the existence of κ_{spin} .

2. Experimental

Single crystals of $\text{Cu}_3\text{Mo}_2\text{O}_9$ were grown by the continuous solid-state crystallization method.³² Thermal conductivity measurements were carried out by the conventional steady-state method. One side of a rectangular single-crystal, whose typical dimensions were about $5 \times 1 \times 1 \text{ mm}^3$, was anchored on a heat sink of copper with indium solder. A chip-resistance of $1 \text{ k}\Omega$ (Alpha Electronics MP1K000) was attached as a heater to the opposite side of the single crystal with GE7031 varnish. The temperature difference across the crystal (0.03 – 0.4 K) was measured with two Cernox thermometers (Lake Shore Cryotronics CX-1050-SD). The accuracy of the absolute value of the thermal conductivity was $\pm 10\%$ mainly due to the uncertainty of the sample geometry. Magnetic fields up to 14 T were applied parallel to the principal crystallographic axes.

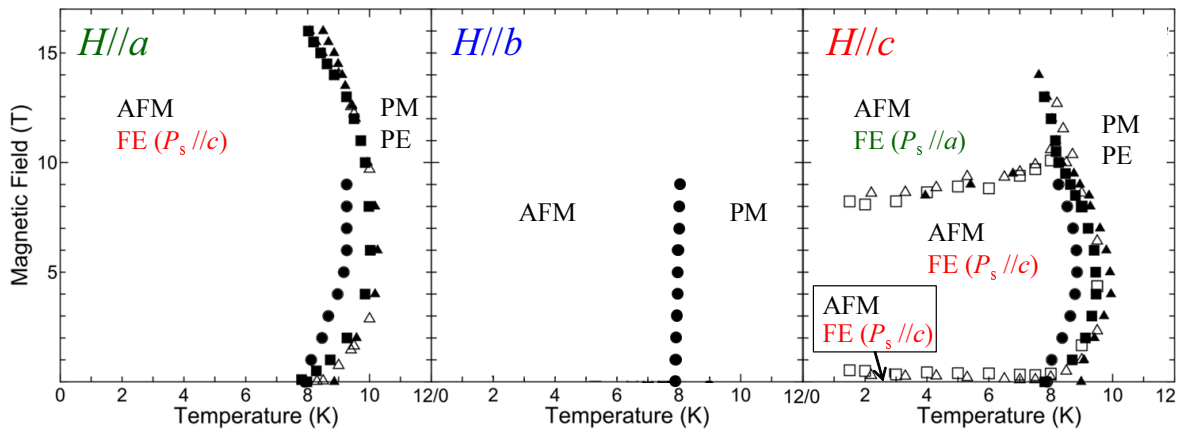


Fig. 2. (Color online) Phase diagram of $\text{Cu}_3\text{Mo}_2\text{O}_9$ in magnetic fields along the principal crystallographic axes at low temperatures.^{26,30,31} AFM, PM, FE, and PE indicate the antiferromagnetic, paramagnetic, ferroelectric, and paraelectric phases, respectively. P_s indicates the spontaneous electric polarization. Triangles, squares, and circles were determined from the dielectric constant measurements along the a - and c -axes and specific heat measurements, respectively. Open and solid symbols were obtained from the data of magnetic-field and temperature dependences, respectively.

3. Results and Discussion

Figure 3 shows the temperature dependence of the thermal conductivity along the a -, b -, and c -axes, κ_a , κ_b , and κ_c , of $\text{Cu}_3\text{Mo}_2\text{O}_9$, respectively. It is found that κ_a and κ_c perpendicular to the spin chains are similar to each other and monotonically decrease with decreasing temperature down to $T_N = 8$ K. Although κ_b parallel to the spin chains also decreases with decreasing temperature down to ~ 20 K, on the other hand, κ_b increases with decreasing temperature from ~ 20 K down to T_N . Both κ_a , κ_b and κ_c increase suddenly just below T_N with decreasing temperature and exhibit a peak at approximately 5 K. In nonmagnetic insulators, κ_{phonon} typically increases with decreasing temperature from room temperature and shows a peak at a low temperature around 10 K. In spin-gap systems, moreover, thermal conductivity typically increases with decreasing temperature at low temperatures below the temperature comparable to the spin-gap energy. Taking into account the observation of the dispersion branch of magnetic excitations of the spin dimers,^{23,24} therefore, the monotonic decrease with decreasing temperature at high temperatures implies that the mean free path of phonons, l_{phonon} , is strongly suppressed probably by magnetic fluctuations due to the spin frustration.

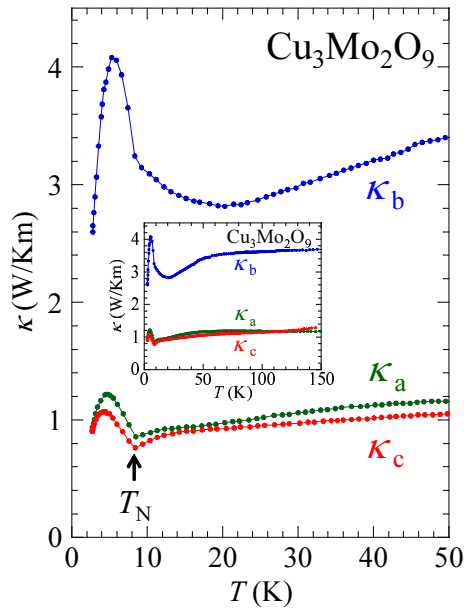


Fig. 3. (Color online) Temperature dependence of the thermal conductivity along the a -, b -, and c -axes, κ_a , κ_b , and κ_c , for $\text{Cu}_3\text{Mo}_2\text{O}_9$ single crystals in zero field, respectively. The inset shows the temperature dependences of κ_a , κ_b and κ_c in a wide temperature-range up to 150 K. The arrow indicates the antiferromagnetic transition temperature, T_N .

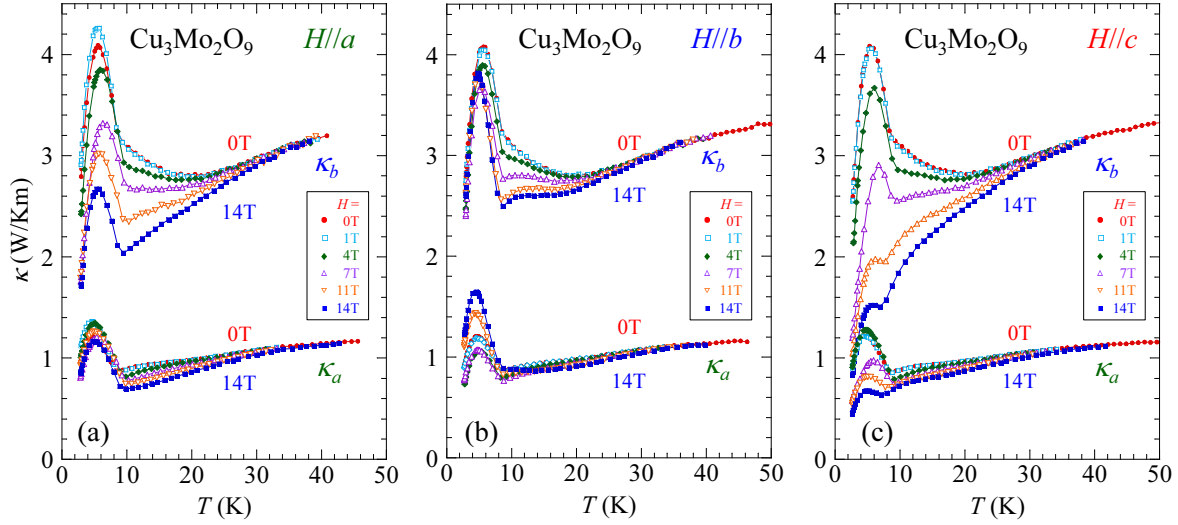


Fig. 4. (Color online) Temperature dependence of the thermal conductivity along the a - and b -axes, κ_a and κ_b , respectively, for $\text{Cu}_3\text{Mo}_2\text{O}_9$ single crystals in magnetic fields parallel to the (a) a -, (b) b -, and (c) c -axes.

The sudden increases in κ_a , κ_b , and κ_c just below T_N are inferred to be due to the increase in l_{phonon} owing to the marked reduction in the phonon-spin scattering rate caused by the development of the AF long-range order, as observed in several antiferromagnets.^{14–20}

It is found that the magnitude of κ_b is larger than those of κ_a and κ_c . Furthermore, only κ_b increases with decreasing temperature at temperatures between ~ 20 K and T_N , which can hardly be explained as being due to the anisotropy of κ_{phonon} . Therefore, these anisotropic behaviors of the thermal conductivity are reasonably attributed to the contribution of κ_{spin} to κ_b , because magnetic excitations can carry heat along the b -axis where the magnetic correlation is developed at low temperatures below J_4 . Such anisotropic contribution of κ_{spin} has been observed in several low-dimensional spin systems.^{1–9, 19, 33–38}

Figure 4 shows the temperature dependences of κ_a and κ_b of $\text{Cu}_3\text{Mo}_2\text{O}_9$ in magnetic fields along the a -, b -, and c -axes, $H_{\parallel a}$, $H_{\parallel b}$, and $H_{\parallel c}$, respectively. It is found that both κ_a and κ_b decrease with increasing field at low temperatures below ~ 40 K. The decrease in κ_a by the application of a magnetic field indicates the decrease in l_{phonon} due to the increase in the phonon-spin scattering rate, namely, the enhancement of the scattering of phonons by magnetic excitations, because the contribution of κ_{phonon} is dominant in κ_a perpendicular to the spin chains and the contribution of κ_{spin} is negligible. It is known in spin-gap systems that κ_{phonon} is enhanced below the temperature comparable to the spin-gap energy, owing to the

marked decrease in the number of magnetic excitations. Moreover, the enhancement of κ_{phonon} is suppressed by the application of a magnetic field,^{10, 12, 13} owing to the increase in the number of magnetic excitations because of the reduction in the spin gap. In the magnetic dispersion of $\text{Cu}_3\text{Mo}_2\text{O}_9$, there is a flat branch of magnetic excitations of the spin dimers.^{23, 24} Such a flat magnetic branch is expected to scatter phonons strongly, because the momentum conservation law is easily satisfied in the phonon-spin scattering process. Surely, κ_{phonon} is suppressed owing to the disorder of the AF correlation induced by the application of the magnetic field in AF spin-chain systems. However, since the magnetic dispersion branch in AF spin-chain systems is dispersive, it is not easy to satisfy both the momentum and energy conservation laws in the phonon-spin scattering process. Therefore, magnetic excitations of the spin dimers are expected to scatter phonons stronger than those of the AF spin chains. Furthermore, considering that the temperature below which the suppression by the application of a magnetic field is observed is comparable to $\Delta = 67 \text{ K}$ ^{23, 24}, the suppression of not only κ_a but also κ_b by the application of a magnetic field is interpreted as being caused by the enhancement of the phonon-spin scattering due to the reduction in the spin gap. However, neither enhancement of κ_a , κ_b , nor κ_c is observed in zero field below $\sim 40 \text{ K}$ comparable to Δ . This may indicate that phonons are strongly scattered by magnetic fluctuations due to the spin frustration even at low temperatures below Δ . Furthermore, the decrease in κ_b by the application of a magnetic field is more marked than that in κ_a . This indicates that not only κ_{phonon} but also κ_{spin} decreases by the application of a magnetic field, because there exists the contribution of κ_{spin} to κ_b parallel to the spin chains in zero field as described above. It is reasonable that κ_{spin} is affected by magnetic fields up to 14 T, because $J_4 \sim 46 \text{ K}$ is not much larger than the energy of a magnetic field of 14 T. Namely, magnetic excitations carrying heat are scattered by the disorder of the antiferromagnetic correlation along the b -axis induced by the application of a magnetic field. In fact, it has been reported that κ_{spin} in the quasi-one-dimensional spin system $\text{Sr}_2\text{V}_3\text{O}_9$ with the intrachain interaction of 82 K is suppressed by the application of a magnetic field of 14 T.^{36, 37} As for the behavior of the thermal conductivity in magnetic fields at low temperatures below T_N , it is slightly complicated.

Figures 5(a)–5(d) show the magnetic-field dependences of $\kappa_a(H)/\kappa_a(0)$, and $\kappa_b(H)/\kappa_b(0)$ of $\text{Cu}_3\text{Mo}_2\text{O}_9$, normalized by the value in zero field, in $H_{\parallel a}$, $H_{\parallel b}$ and $H_{\parallel c}$ at 3 and 10 K. First, we compare $\kappa_a(H)/\kappa_a(0)$ and $\kappa_b(H)/\kappa_b(0)$. It is found that both $\kappa_a(H)/\kappa_a(0)$ and $\kappa_b(H)/\kappa_b(0)$ show a complicated but similar behavior in general terms, but $\kappa_b(H)/\kappa_b(0)$ tends to decrease with increasing field more than $\kappa_a(H)/\kappa_a(0)$. Here, κ_b parallel to the spin chains is described as the sum of κ_{phonon} and κ_{spin} , while κ_a perpendicular to the spin chains is given by only κ_{phonon} .

Therefore, it is inferred that the complicated field-dependence of the thermal conductivity is due to κ_{phonon} , while κ_{spin} monotonically decreases with increasing field, as shown in Fig. 5(e).

Next, we discuss the magnetic-field dependence of $\kappa_a(H)/\kappa_a(0)$ in order to investigate the

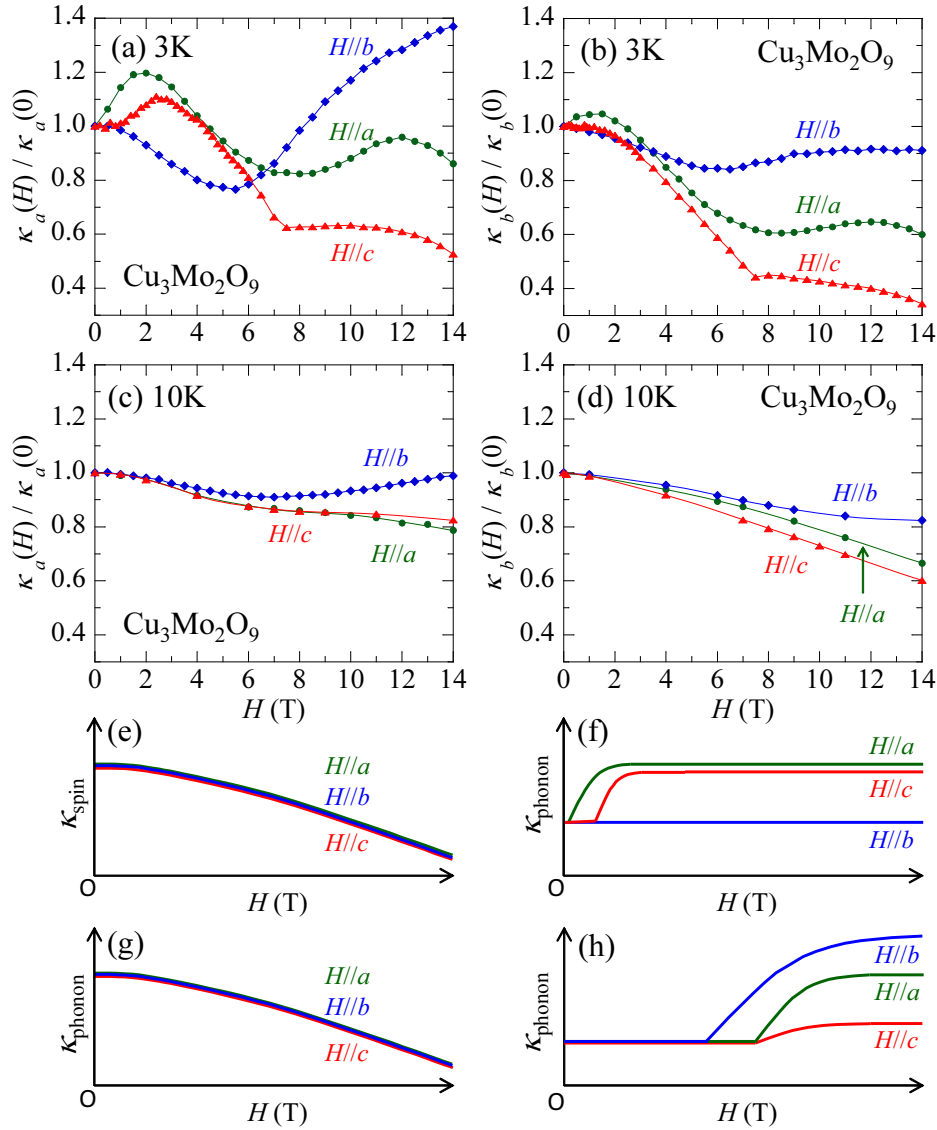


Fig. 5. (Color online) (a)–(d) Magnetic-field dependence of the thermal conductivity along the a - and b -axes normalized by the value in zero field, $\kappa_a(H)/\kappa_a(0)$ and $\kappa_b(H)/\kappa_b(0)$, respectively, for $\text{Cu}_3\text{Mo}_2\text{O}_9$ single crystals in magnetic fields parallel to the a -, b -, and c -axes at 3 and 10 K. (e)–(h) Schematic diagrams of the magnetic-field dependence of the thermal conductivity due to magnetic excitations, κ_{spin} , and phonons, κ_{phonon} . (e) κ_{spin} suppressed by the reduction in the spin gap. (f) κ_{phonon} enhanced by the appearance of the long-range order of the canted components in the weak ferromagnetic state. (g) κ_{phonon} suppressed by the reduction in the spin gap. (h) κ_{phonon} enhanced in high magnetic fields.

magnetic and dielectric states, because the behavior of $\kappa_a(H)/\kappa_a(0)$ originating from only κ_{phonon} is expected to reflect these states through the scattering of phonons more simply than that of $\kappa_b(H)/\kappa_b(0)$. It is found that the field dependence of $\kappa_a(H)/\kappa_a(0)$ at 3 K is very different depending on the applied-field-direction, as shown in Fig. 5(a). In low magnetic fields, $\kappa_a(H)/\kappa_a(0)$ increases up to ~ 2 T with increasing fields of $H_{\parallel a}$ and $H_{\parallel c}$, while it decreases up to ~ 5 T with increasing field of $H_{\parallel b}$. Since the long-range order of canted components of the magnetic moments in WF appears above $H_{\parallel a} \sim 0.1$ T and $H_{\parallel c} \sim 0.8$ T but it does not in $H_{\parallel b}$,²⁶ the increase in $\kappa_a(H)/\kappa_a(0)$ with increasing fields of $H_{\parallel a}$ and $H_{\parallel c}$ is explained as being caused by the appearance of the long-range order of the canted components in WF leading to the suppression of the phonon-spin scattering. Therefore, there is an enhanced component of κ_{phonon} in both $H_{\parallel a}$ and $H_{\parallel c}$, as shown in Fig. 5(f). The decrease in $\kappa_a(H)/\kappa_a(0)$ in $H_{\parallel b}$ is explained as being caused by the increase in the phonon-spin scattering rate due to the reduction in the spin gap by the application of a magnetic field. Furthermore, it is found that $\kappa_a(H)/\kappa_a(0)$ starts to decrease above ~ 2 T with increasing fields of $H_{\parallel a}$ and $H_{\parallel c}$, which is interpreted as being caused by both the saturation of the enhancement of $\kappa_a(H)/\kappa_a(0)$ by the appearance of the long-range order of the canted components in WF, as shown in Fig. 5(f), and the decrease in $\kappa_a(H)/\kappa_a(0)$ due to the reduction in the spin gap, as shown in Fig. 5(g).

In high magnetic fields, $\kappa_a(H)/\kappa_a(0)$ tends to increase above ~ 7 T with increasing fields of $H_{\parallel a}$, $H_{\parallel b}$, and $H_{\parallel c}$, as shown in Fig. 5(a). In particular, it is remarkable that there is a kink in $\kappa_a(H)/\kappa_a(0)$ at $H_{\parallel c} \sim 7.5$ T, where the phase transition occurs, that is, the direction of the spontaneous electric polarization changes from the c -axis to the a -axis with increasing field, as shown in Fig. 2.²⁶ A similar kink is also observed in $\kappa_b(H)/\kappa_b(0)$ at $H_{\parallel c} \sim 7.5$ T. In $H_{\parallel a}$ and $H_{\parallel b}$, on the other hand, no anomaly suggesting any phase transitions has been observed at around 7 T in the specific heat³⁰ and magnetization³⁹ measurements. However, since the differential magnetization has shown a kink at $H_{\parallel b} = 6$ T at 2 K, the enhancement of $\kappa_a(H)/\kappa_a(0)$ above ~ 7 T may be caused by an unknown field-induced order and/or a change in the magnetic state. Accordingly, there is an enhanced component of κ_{phonon} in $H_{\parallel a}$, $H_{\parallel b}$, and $H_{\parallel c}$, as shown in Fig. 5(h). The enhancement of $\kappa_a(H)/\kappa_a(0)$ above ~ 7 T is also observed at 10 K above T_N , as shown in Fig. 5(c).

Here, it is noted that the enhancement of $\kappa_a(H)/\kappa_a(0)$ above ~ 7 T means the increase of l_{phonon} , because both the specific heat and velocity of phonons are usually almost independent of magnetic field. In other words, it means that the scattering rate of phonons decreases with increasing field, corresponding to the decrease in magnetic excitations and/or the development of a magnetic order. According to the calculation of the magnetic dispersion in

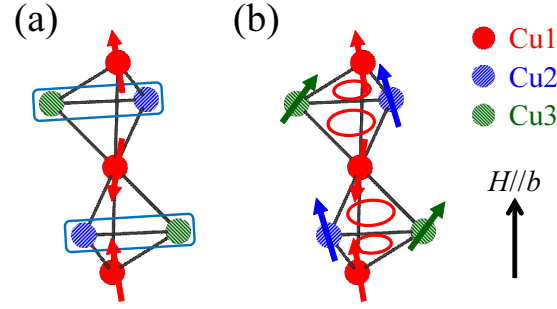


Fig. 6. (Color online) Schematic diagram of spin chiralities and spontaneous currents caused by the break of dimers of Cu2 and Cu3 in $\text{Cu}_3\text{Mo}_2\text{O}_9$. (a) In the case that spins of Cu2 and Cu3 form a spin-singlet dimer, there is no chirality in the spin chain. Rounded rectangles and arrows indicate spin-singlet dimers and spins on the Cu1 site, respectively. (b) In a magnetic field along the b -axis, spontaneous currents run along triangles composed of three Cu spins, owing to the break of spin-singlet dimers. Open ovals and arrows indicate spontaneous currents and spins, respectively.

magnetic fields by Matsumoto *et al.*,⁴⁰ no anomaly such as any change in the ground state has been suggested at ~ 7 T.

Here, in order to explain the enhancement of κ_{phonon} above ~ 7 T, we introduce the theory proposed by Bulaevskii and Batista²⁷ and Khomskii²⁸ concerning spontaneous currents and charge redistribution in a Mott insulator regarded as a geometrically frustrated spin system. Since the ferroelectricity in $\text{Cu}_3\text{Mo}_2\text{O}_9$ has been understood on the basis of the charge redistribution,²⁶ the spontaneous currents may be useful to explain the enhancement of κ_{phonon} . In a geometrically frustrated Mott insulator, the exchange interaction between three spins forming a triangle causes a spontaneous current running along the triangle. This spontaneous current only appears in a non-coplanar spin-state and is proportional to the scalar spin-chirality given by $\mathbf{S}_1 \cdot (\mathbf{S}_2 \times \mathbf{S}_3)$, where \mathbf{S}_i ($i = 1, 2, 3$) is a spin angular momentum on the site i . In the case that the spins of Cu2 and Cu3 form a spin-singlet dimer, distorted tetrahedral spin-chains can be regarded as simple spin-chains composed of only Cu1 spins and there is no chirality in the spin chain, as shown in Fig. 6(a). In the case that spin-singlet dimers are broken by the application of a magnetic field, on the other hand, finite values of spin chirality appear in the triangles, because spins revive on the Cu2 and Cu3 sites, as shown in Fig. 6(b). Therefore, it is possible that the enhancement of κ_{phonon} above ~ 7 T is caused by the ordering of spin chiralities, because the ordering is able to be brought about by the magnetic interaction even in the absence of any magnetically ordered state.

Finally, the magnetic-field dependence of $\kappa_a(H)/\kappa_a(0)$ at low temperatures below ~ 40 K

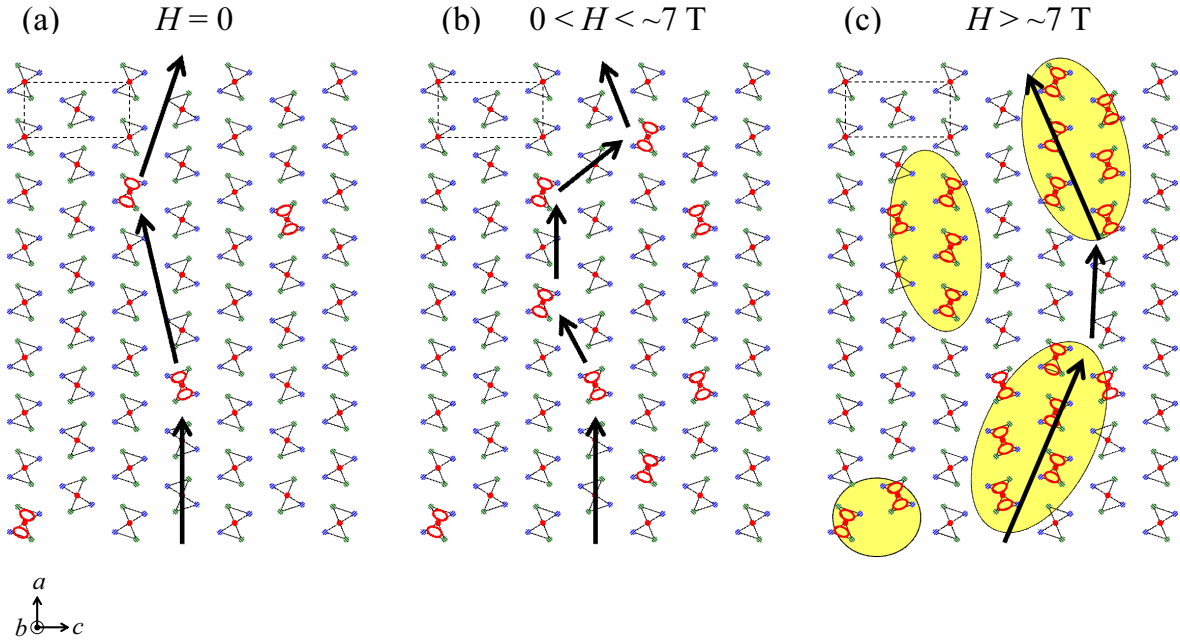


Fig. 7. (Color online) Schematic diagram of the development of the spin-chirality order in $\text{Cu}_3\text{Mo}_2\text{O}_9$. Open ovals and the length of arrows indicate excitations of spin-singlet dimers and the mean free path of phonons, l_{phonon} , respectively. (a) In zero field, the magnitude of l_{phonon} is limited by magnetic excitations generated by thermal fluctuations. (b) In low magnetic fields below ~ 7 T, the number of magnetic excitations increases with increasing field because of the reduction in the spin gap, so that l_{phonon} is shortened because of the increase in the phonon scattering rate. (c) The spin-chirality order is developed above ~ 7 T, so that l_{phonon} extends because of the decrease in the phonon scattering rate. Filled ovals indicate areas of the spin-chirality order.

is summarized as follows, on the basis of the scenario adopting the spin-chirality ordering. In zero field, a few excitations of spin-singlet dimers in the spin-gap state due to thermal fluctuations scatter phonons, as shown in Fig. 7(a). Since the number of magnetic excitations increases with increasing field below ~ 7 T by the reduction in the spin gap, l_{phonon} is shortened because of the increase in the phonon scattering rate, as shown in Fig. 7(b). In high magnetic fields above ~ 7 T, the order of magnetic excitations, namely, the order of spin chiralities, is developed, as shown in Fig. 7(c), so that κ_{phonon} increases owing to the decrease in the phonon scattering rate. The reason why the enhancement of $\kappa_a(H)/\kappa_a(0)$ is different depending on the applied-field-direction is as follows. Spontaneous currents along the triangles composed of three spins induce orbital moments, which are coupled with the magnetic field. Therefore, the magnitude of the scalar spin-chirality might be related to the magnetic field penetrating the triangles. Accordingly, since the areas of the triangles viewed from the b -axis are homogeneous, the chirality order may be homogeneous in $H_{\parallel b}$, leading to

the large enhancement of κ_{phonon} . On the other hand, since the areas of the triangles viewed from the a - and c -axes are inhomogeneous, the chirality order may be inhomogeneous in $H_{\parallel a}$ and $H_{\parallel c}$, leading to the small enhancement of κ_{phonon} . To confirm this scenario adopting the spin-chirality order, further experimental and theoretical investigations are necessary.

4. Summary

In order to investigate the magnetic state and the existence of κ_{spin} , we have measured κ_a , κ_b , and κ_c of $\text{Cu}_3\text{Mo}_2\text{O}_9$ single crystals in magnetic fields up to 14 T. In zero field, it has been found that κ_a , κ_b , and κ_c are suppressed at high temperatures probably by magnetic fluctuations due to the spin frustration, while they are enhanced just below T_N as in the case of several antiferromagnets. By the application of a magnetic field, κ_a , κ_b , and κ_c have been found to be suppressed at low temperatures below ~ 40 K and this has been explained as being due to the reduction in the spin gap originating from the spin-singlet dimers of Cu2 and Cu3. Since it has been found that the magnitude of κ_b parallel to the spin chains is larger than those of κ_a and κ_c and that the decrease in κ_b by the application of a magnetic field is more marked than that in κ_a , it is concluded that there exists a contribution of κ_{spin} to κ_b . Furthermore, it has been found that the magnetic-field dependences of κ_a and κ_b at 3 and 10 K are complicated and different depending on the applied-field-direction. In low magnetic fields below ~ 7 T, both κ_a and κ_b have been found to decrease with increasing field due to the reduction in the spin gap. Moreover, κ_a at 3 K has been found to markedly change in $H_{\parallel a}$ and $H_{\parallel c}$ in correspondence to the appearance of the long-range order of the canted components in WF. In high magnetic fields above ~ 7 T, on the other hand, both κ_a and κ_b at 3 K have been found to tend to increase with increasing field. In $H_{\parallel c}$, a kink has been observed at ~ 7.5 T in both κ_a and κ_b , owing to the field-induced phase transition. In $H_{\parallel b}$, it has been found that the increase in κ_a above ~ 7 T is most marked and is observed even at 10 K above T_N in spite of the absence of any phase transition, suggesting the existence of a novel field-induced spin state. A possible state is the ordered one of the spin chirality in a frustrated Mott insulator.

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